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Fourth Quarterly Report

Development of Uniform and Predictable Battery Materials For Nickel-Cadmium Aerospace Cells

(8 February 1969— 7 May 1969)

Contract No.: NAS5-11561

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Prepared by

Tyco Laboratories, Inc.
Bear Hill
Waltham, Massachusetts 02154

for

Goddard Space Flight Center
Greenbelt, Maryland

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ABSTRACT

This report describes the preparation of nickel-cadmium battery plaques by coating a 20-mesh nickel screen with a slurry of nickel powder in a methyl cellulose solution. There were 23 preparations made in a semicontinuous process. The following variables were studied: nickel powder type, ratio of nickel powder to methyl cellulose in the slurry, doctor blade setting, pulling speed, and screen thickness. The plaques ranged in thickness from 0.014 to 0.031 in., and the preferred slurry viscosity was close to 1×10^5 cps. Selected plaques were examined for uniformity across the width of the screen and along the direction of pulling. Very good uniformity was obtained across the width, e.g., less than 0.2% variation in porosity and no variation of surface area within the accuracy of the measurement. A 0.5% variation in porosity was observed between the first and last plaques of a single pulling operation.

A sample of BASF carbonyl nickel powder was characterized and was found to be similar to INCO type 255 powder.

I. INTRODUCTION

The overall objective of this project is to establish a systematic procedure to produce uniform components for nickel-cadmium cells for aerospace use.

Following current practice throughout the nickel-cadmium battery industry, we have confined our approach to a study of battery plaques prepared by the sintering of carbonyl nickel powders.

Work carried out prior to this report period has shown that there are significant variations in the physical characteristics of carbonyl nickel powder from batch to batch. The influences of these variations and of the variables in the sintering process were established in loose sintering studies (the details of this work are described in the Third Quarterly Report). Probably the most important point to emerge was that loose sintering does not produce a uniform plaque.

Because of this lack of uniformity, and also to conform more closely to the large scale production process for nickel plaque fabrication, we have progressed to a semicontinuous slurry coating technique. The present report describes this process and the physical characteristics of the plaques produced.

II. SLURRY COATING PROCESS

This process consists of the preparation of a suspension of carbonyl nickel powder in a viscous medium; in this particular case, a 3% solution of methyl cellulose (Dow Chemical Co., Methocel 90 HG) in water which is then used to coat a 20-mesh nickel screen. The methyl cellulose acts as a binder until the sintering process. It also has the special advantage that it burns in the sintering furnace to leave very little residue (<0.1% by weight).

The method of preparation consisted of the combination of the required weight of Methocel with 2/3 of the required water at 90 °C. This solution was stirred for about 5 min to thoroughly wet the Methocel powder. The remaining water was then added cold, and the solution cooled to ~ 5 °C with stirring to effect complete dissolution. Without the cooling step, a cloudy solution was obtained. After 20 min at 5 °C, the solution was warmed to 25 °C.

There are two principal problems associated with the preparation of the nickel slurry with the Methocel solution: (1) avoiding entrainment of air (which causes blistering of the plaque on sintering). and (2) attaining a homogeneous slurry without damaging the rather fragile nickel particles.

The procedure adopted was to evacuate a chamber containing dry nickel powder, introduce the Methocel solution to this chamber, and then admit air to force the solution into the powder. At this point, the wet mix was stirred with a Brookfield counter-rotating mixer for 10 min to produce a homogeneous slurry. The small quantity of air remaining in the slurry was removed by reducing the pressure for 10 min while stirring slowly. After completion, the viscosity of the slurry was measured.

The variables in the process that were examined during this report period were the type of nickel powder and the weight content of nickel in the slurry.

The application of the nickel slurry to the screen was accomplished by pulling the screen under rollers in a box containing the slurry. The apparatus was so arranged that the screen passed under a roller at one

end of the box and moved horizontally through the slurry to effect continual stirring. The screen was then pulled up vertically over the other roller and the excess slurry trimmed off between two variable doctor blades. Finally, as the slurry coated screen moved upwards, it passed between infrared lamps for drying. In this way, about 6 ft of green plaque were obtained in each run (see Fig. 1).

The pulling speed could be adjusted from about 1 to 30 in./min. Most runs were made at about 9 in./min to allow sufficient time for drying. The doctor blades were spaced from 30 to 70 mils apart for various runs in an effort to achieve the desired finished plaque thickness. The drying lamps could be adjusted in number and in proximity to the plaque. Initially, four lamps were used at a distance of about 12 in. Later, this was changed to eight lamps at a distance of about 8 in.

All plaques were sintered in pure hydrogen for varying times and temperatures. (The sintering furnace has a flat temperature profile of about 20 in. at 900 °C, and will accommodate 6-in.-wide plaque.)

The plaques were sintered as 6- by 12-in. segments suspended on a graphite rack. The introduction of the plaques into the hot zone of the furnace caused a temperature depression of about 40 °C. By presetting the furnace ~ 25 °C higher than required, the desired temperature was achieved and maintained within 8 to 10 min.

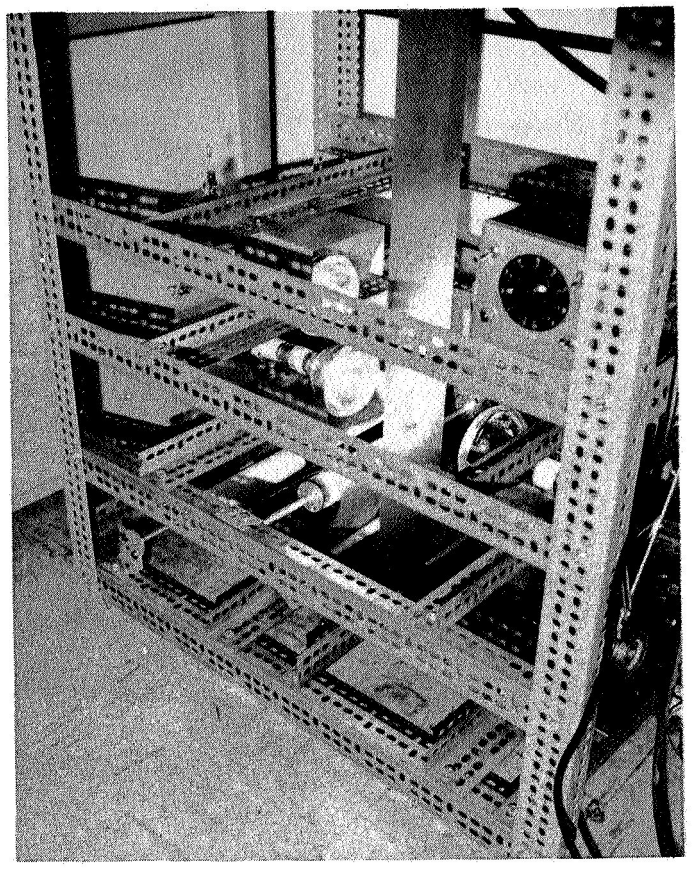

Fig. 1. Slurry coating apparatus

III. PLAQUE PREPARATION

All of the plaques except S-14 were made with INCO 255 nickel powder. The primary parameter studied was the nickel-Methocel ratio and its effect on viscosity. The adjustments of other parameters such as screen thickness, doctor blade setting, and pulling speed were directed toward achieving a uniform plaque of specified thickness (28 mils) within the limits of each slurry (see Table I).

The viscosities* achieved by changes in the nickel-Methocel ratio are given in Table II.

Table II. Variation of Viscosity of Slurry With Nickel Content

Nickel, g per 100 ml Methocel	Viscosity at 25 °C, cps x 10^2	
60	126	
70	184	
80	285	(22.5 °C)
90	310	(23 °C)
100	816	(average of 15 preparations)
120	1540	(spindle LV-3)

The first six runs (up to 90 g nickel/ 100 ml Methocel) were made on a screen of 14-mil overall thickness. The first two runs were exploratory with regard to the removal of air from the slurry. Thereafter, it was found that a plaque thickness could not be attained much in excess of the screen thickness in spite of increasing viscosity. The doctor blades were not limiting in these runs, i.e., the screen carried very little excess slurry.

In the subsequent runs, a screen of 24-mil overall thickness was used and the nickel-Methocel ratio was increased to 100 g nickel/ 100 ml Methocel. With the doctor blades set at 40 mils, it was again found that

*Measured with a Brookfield Viscometer, type LVT.

Table I. Plaque Preparation Conditions

Run No., 255 Powder	Nickel-Methocel*	Viscosity at 25 °C, cps: Methocel	Viscosity at 25 °C, cps: Slurry † x 10^4	Doctor Blade Setting, mils	Pulling Speed ‡	Plaque Thickness, mils	Comments
							Screen pretreated with Triton X-100
S-1	60	1700	1.77	30	2.5	14.5	14-mil screen; air not removed from slurry
S-2	60	—	18.8	40	2.0	18.5	Excessive water evaporation
S-3	60	1412	1.26	40	1.5	15.2	Complete air removal
S-4	70	1200	1.84	45	2.0	17.5	
S-5	80	1267	2.85 at 23 °C	45	2.5	16.5	
S-6	90	1322	3.1 at 23 °C	45	2.5	16.7	
S-7	100	1342	8.3	40	2.5	23	Changed to 24-mil screen
S-8	100	1612	8.75	40	2.5	24.5	
S-9	100	1087	8.75	52	2.5	26	
S-10	100	1175	6.7	52	3.0	26	
S-11	120	1307	15.4	62	3.0	30	Increased drying lamp capacity
S-12	100	1317	8.65	52 62	3.5	27 31	
S-13	100	1450	9.0	52	3.0	26.5	

* Nickel powder, g/100 ml, 3 wt % Methocel.

† All viscosity measurements made with viscometer spindle LV-2, except runs S-11 (LV-3) and S-14 (LV-4). See discussion in text.

‡ Pulling speed equals about 3 in./min/scale unit.

Table I (Cont.)

Run No., 255 powder	Nickel-Methocel	Viscosity at 25 °C, cps		Doctor Blade Setting, mils	Pulling Speed	Plaque Thickness, mils	Comments
		Methocel	Slurry x 10^4				
S-15	100	1100	6.75	57	3.0	—	Room temperature in excess of 30 °C, affecting viscosity
S-16	100	1350	7.2	57	3.0	27	
S-17	100	1437	7.75	57	3.0	27.5	Slurry preparation in temperature controlled chamber
S-18	100	1487	8.0	62	3.0	28	Blemishes from silicone grease
S-19	100	1125	7.85	62	3.0	27.2	Blemishes
S-20	100	1437	7.95	62	3.0	27.8	Blemishes
S-21	100	1437	9.7	62	3.0	27.9	Blemishes
S-22	100	1400	8.0	62	3.0	27.9	Silicone grease found in slurry
S-23	100	1487	9.1	60	3.0	27.8	
287 powder							
S-14	157§	1275	6.2	57	3.0	28.5	

§ Volume of type 287 nickel powder equivalent to g 255 nickel powder, e.e., 157 g nickel/100 ml methocel.

the thickness of the plaques did not exceed the thickness of the screen. The doctor blades were then set at 52 mils for S-9, and an increase in plaque thickness over the thickness of the screen was achieved (~ 26 mils overall). In the next run, S-10, the doctor blades were set at 62 mils, but the slurry started to flow on the screen and the doctor blades had to be reset at 52 mils. It was at this point that it was decided to increase the nickel content to 120 g nickel/ 100 ml Methocel.

Also, at this time the infrared drying lamp arrangement was changed from two lamps staggered vertically to four lamps triangulated at the plaque (i.e., eight lamps, two banks of two on each side). This slurry was run with the doctor blades set at 62 mils. The resulting plaques had an overall thickness of ~ 30 mils which was more than the desired thickness of 28 mils (the sintered plaque showed some "mud-cracking"). It was believed at this time that the change in the drying lamp arrangement was more significant than the viscosity increase. In view of this, and the difficulty in handling the high viscosity slurry, the subsequent runs were made with 100 g nickel/ 100 ml Methocel. In run S-12, it was found that the 100 g nickel/ Methocel ratio slurry could be run with the doctor blades at 62 mils, indicating that the change in the drying lamp arrangement was significant.

In the succeeding runs, refinements were attempted and it was hoped that a number of good runs could be made for possible impregnation with active material. However, a number of difficulties were encountered at this time. Starting with run S-15, the room temperature was in excess of 30 °C, so the temperature of the slurry had to be lowered to 25 °C before running. This had the effect of allowing settling of the slurry to occur during the temperature adjustment with the resultant viscosity gradients. In order to avoid this, a temperature controlled chamber was used for the preparation of the slurry, starting with run S-17. This was successful and, in the succeeding runs, the plaque thickness was brought to almost exactly 28 mils by adjusting the doctor blades to 57 and then 62 mils. However, coincident with the introduction of the temperature controlled chamber, mysterious blemishes began to appear on the plaques. These were obviously not air bubbles and they

only became apparent as the plaque passed through the drying lamps. Since these appeared to be due to local changes in surface tension, it was thought that the wetting agent applied to the screen might be at fault. This was not the case, however, and it was discovered in run S-22 that silicone grease was getting into the slurry by way of a vacuum release stopcock on the temperature controlled chamber. The silicone grease was found to be capable of producing such blemishes on the plaque. When this problem was eliminated, the blemishes disappeared, and run S-23 was very nearly perfect in appearance and thickness.

One run, S-14, was made with type 287 nickel powder. The nickel-Methocel ratio was derived from the 255 nickel/Methocel ratio on an equivalent volume basis. Specifically, this was 157 g type 287 nickel/100 ml Methocel, which is equivalent to the nickel powder volume of 100 g type 255 nickel/100 ml methocel.

The resultant slurry had a viscosity in excess of the equivalent 255 nickel slurry. Since the viscosity could not be measured with the same viscometer spindle (LV-2, 1×10^5 cps maximum), the relative viscosity is not known. The viscosity using LV-2 was in excess of 1×10^5 cps, but the viscosity measured with LV-4 was 6.2×10^4 cps. By comparison with S-13, which showed a viscosity of 9×10^4 cps with LV-2 and 3.2×10^4 cps with LV-4, S-14 would have a relative viscosity of $\sim 1.75 \times 10^5$ cps. By comparison with S-12, which showed a viscosity of 8.65×10^4 cps with LV-2 and 5.4×10^4 cps with LV-4, the relative viscosity of S-14 would be $\sim 1 \times 10^5$ cps. Hence, it can be seen that there are serious difficulties in determining even the relative viscosities of these slurries. The plaque derived from S-14 was reasonably good in all respects, except for some "mud-cracking." Future runs with type 287 nickel powder will be carried out with lower nickel content.

No problems were experienced in the sintering of the plaques, except for a slight difference in thermal lag in the furnace with the replacement of a faulty solenoid valve. The various sintering conditions for the plaques are given in Table III. The plaques were sintered in 13-in. lengths which were lettered consecutively A through F in the direction of coating of the plaque. The complete identification code for the physical characterization is given in Fig. 2.

Table III. Sintering Conditions, Plaques S-7 to S-12

	Temperature, °C/Time, Min					
	A	B	C	D	E	F
S-7	900/30*	900/15	900/60	800/30	900/30	
S-8	900/30	900/15	900/60	800/30	900/30	
S-9	900/30				900/30	
S-10	900/30	900/30	900/30	900/30		
S-11	900/30	900/15	900/15	900/30		900/30
S-12			900/15	900/30		
S-13	900/30	900/15	900/60	900/30	800/60	900/30
S-14	900/30	900/60		900/30	800/15	900/30
S-15			Did not sinter			
S-16		900/30		900/30		900/30
S-17		900/30		900/30		900/30
S-18				900/30		
S-19				900/30		
S-20				900/30		
S-21				900/30		
S-22				900/30		
S-23		900/30	900/60	900/30	800/15	900/30

After drying, the slurry coated screen is cut into five or six 13-in. pieces, depending on total length, that are lettered sequentially.

* Brace indicates that these samples were sintered simultaneously.

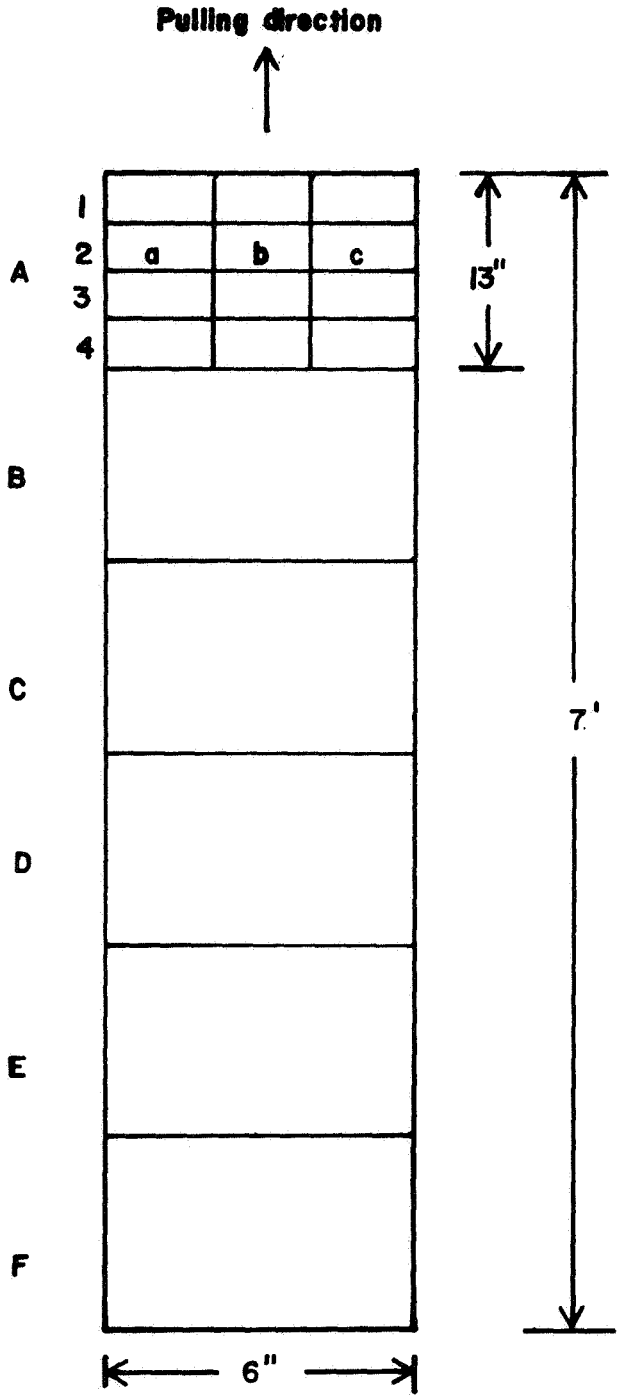

Fig. 2. Identification code for plaque physical characterization

IV. PHYSICAL CHARACTERISTICS AND UNIFORMITY OF PLAQUES

Three of the plaques prepared during this report period were chosen for characterization. More extensive characterization is intended when the slurry coating process has been perfected. The plaques examined were S-6, S-13, and S-14. S-6, prepared from type 255 powder, was chosen for comparison with two commercial samples of plaque based on 20-mesh, 0.014-in.-thick screen. S-13 and S-14 were prepared on 20-mesh, 0.024-in.-thick screen, the former using type 255 powder, the latter 287.

Before discussing these results, it is necessary to comment on the differences in structure of the materials being compared. Typical cross sections of the Tyco and commercial plaques are shown diagramatically in Fig. 3. Note that only in commercial sample no. 2 can a sensible measurement of the thickness be made. For the other two samples, shrinkage during sintering has resulted in the porous mass becoming recessed in the screen. The screen then interferes with any direct measurement of thickness and hence the porosity. This measurement is therefore not a good criterion for uniformity, particularly for the Tyco prepared material. (Note that more recently prepared plaques have a porous mass substantially thicker than the screen so that this problem is minimized.) We can, however, measure porosity directly using the mercury porosimeter. Also, by using the volume of the plaque obtained from the porosimetry measurements, it is possible to calculate the real thickness of the porous mass. In the case of the Tyco material, it is necessary to subtract the volume of the screen and then divide by its open area to determine the real thickness of the porous mass. These measurements are presented in parentheses in Tables IV and V. Note also that the porosities are in all cases corrected for the presence of the nickel support screen in order to make the figures more sensitive in comparisons to test uniformity.

In the case of the Tyco plaque S-6, two pieces (A and E) were examined for uniformity along the length of the plaque. Uniformity across the 6-in. width was compared in terms of three 2-in. strips designated a, b, and c, from left to right (see Fig. 2).

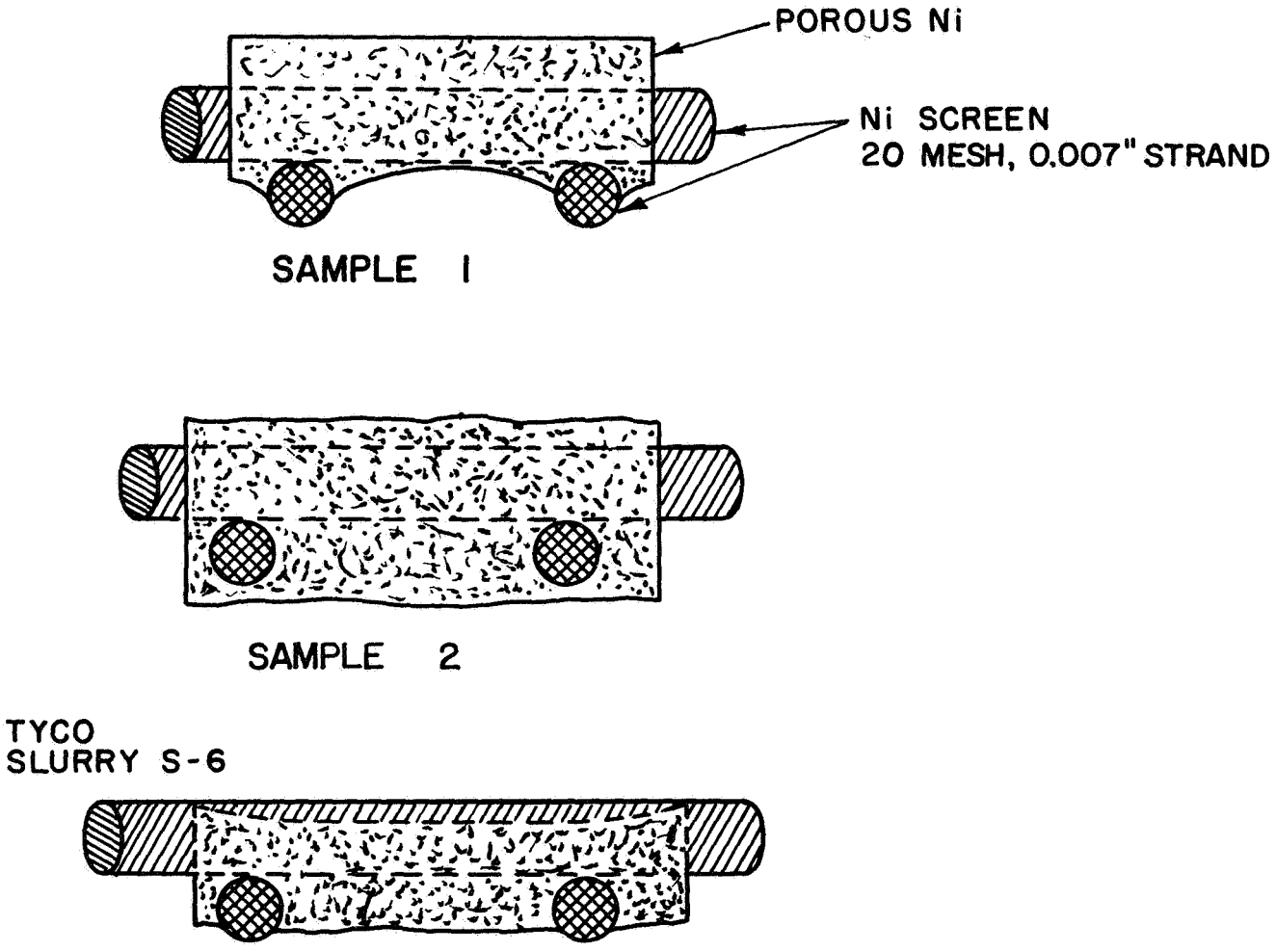

Fig. 3. Cross section of commercial and Tyco nickel plaques

Table IV. Physical Characteristics of Plaque S-6

Identification	Thickness, in.	Porosity, %*	Resistivity, ohm, cm x 10^{-4}	Mechanical Strength, kg/cm^2	Surface Area m^2/g
A-2a	0.0165	86.01	0.90	89.1	0.101
A-2b	0.0163 (0.0137)†	86.00 (62.63)	0.99	87.3	0.096
A-2c	0.0167	85.84	0.90	87.0	0.094
E-2a	0.0165	85.14	0.94	90.9	—
E-2b	0.0168	85.82	0.97	91.4	—
E-2c	0.0167	85.55	0.87	92.5	—

* Porosity of porous mass, i.e., corrected for the presence of the screen.

† Figures in parentheses derived from mercury porosimetry data.

Table V. Physical Characteristics of Commercial Plaques

Identification	Thickness, in.	Porosity, %*	Resistivity, ohm cm x 10^{-4}	Mechanical Strength, kg/cm^2	Surface Area m^2/g
Sample 1					
a	0.0234	81.75	1.43	65.5	0.144
b	0.0242	81.94	1.41	63.9	0.118
c	0.0244	81.62	1.40	70.8	0.141
d	0.0223	82.18	1.29	57.8	0.149
e	0.0223 (0.0213)†	82.93 (81.61)	1.13	59.4	
f	0.0227 (0.0223)	82.99 (82.63)	1.11	59.4	
Sample 2					
a	0.0287	81.83	1.00	125.5	0.138
b	0.0285	81.42	0.94	128.2	0.127
c	0.0288	81.56	1.16	124.9	0.127
d	0.0290	81.07	0.98	128.5	0.131
e	0.0293 (0.0275)	80.80 (79.76)	0.88	129.0	
f	0.0293 (0.0250)	81.67 (78.78)	0.94	121.0	

* Porosity of porous mass, i.e., corrected for the presence of the screen.

† Figures in parentheses derived from mercury porosimetry data.

As may be noted from Table IV, the plaque showed good uniformity across the width with respect to porosity (the figures ranged from 85.8 to 86.0% for A-2 and 85.1 to 85.8% for E-2). These figures represent apparent porosities calculated from the nominal thickness; the real porosity measured for A-2b was 62.6%. The slight decrease in porosity from A to E of about 0.5% probably represents an increase in the solid content of the slurry in the course of the slurry coating process. Note that a decrease in the porosity of 0.5% corresponds to an increase of approximately 3% in the weight of nickel per unit area of electrode — a significant increase. This is reflected by an increase in mechanical strength, although the resistivity remains remarkably uniform. Surface area was measured only for A-2 in this preliminary analysis. Good uniformity across the width of the plaque is apparent.

The measurements made on the commercial plaques are recorded in Table V. For these materials, the identification letters refer to two groups of samples: a, b, and c were from one region of the plaque, d, e, and f from another. The first sample shows a 1% variation in porosity between the two regions, the second sample shows no significant change. The real porosities in parentheses are significantly higher than the Tyco material. The resistivity and surface area of sample 1 are higher than that of the Tyco material, and it has a lower mechanical strength indicating less vigorous sintering conditions. The measured resistivities are, however, inconsistent with the porosity and mechanical strength data: the plaque with the lower porosity apparently has the higher resistivity.

For the second commercial sample, even though the real porosity is higher than that of the Tyco material, the resistivity is comparable and the mechanical strength higher. The resistivity, mechanical strength, and surface area show very good uniformity.

The data obtained for plaques S-13 and S-14 are presented in Tables VI and VII. For these materials, sufficient porosimetry measurements were made to indicate that in both cases the real thickness of the porous mass increased as the slurry coating process progressed. The effect was more marked for S-14, with 0.004-in. increase. The mechanical

Table VI. Physical Characteristics of Plaque S-13

Identification	Thickness, in.	Porosity, %	Resistivity, ohm, cm x 10^{-4}	Mechanical Strength, kg/cm^2	Surface Area m^2/g
A-1a	0.0262		0.70	95.3	0.103
A-1b	0.0262 (0.0178)*	(76.39)	0.72	92.2	0.096
A-1c	0.0262		0.64	91.2	0.107
D-2a	0.0253		0.63	105.5	0.111
D-2b	0.0253 (0.0192)	(78.02)	0.70	105.6	0.108
D-2c	0.0260 (0.0191)	(77.73)	0.68	101.9	0.100

*Figures in parentheses derived from mercury porosimetry data.

Table VII. Physical Characteristics of Plaque S-14

Identification	Thickness in.	Porosity, %	Resistivity, ohm, cm x 10^{-4}	Mechanical Strength, kg/cm^2	Surface Area m^2/g
A-4a	0.0296		0.57	150.4	0.110
A-4b	0.0296 (0.0204)*	(75.16)	0.60	138.4	0.108
A-4c	0.0294		0.58	140.3	
D-2a	0.0296		0.56	156.5	
D-2b	0.0294 (0.0240)	(75.40)	0.57	167.7	
D-2c	0.0293		0.59	150.5	

* Figures in parentheses derived from mercury porosimetry data.

strength measurements reflected the difference in the thickness, but the resistivity and surface area were quite uniform.

The porosity of the 255 plaques (S-13) were slightly higher than those of the 287; both are more porous than S-6 described above. The 255 plaques also showed higher resistivity and lower mechanical strength, as would be expected for the plaque of higher porosity.

Cursory examination of the effect of sintering conditions on plaque properties for S-13 and S-14 indicates that the behavior is somewhat different from that observed for loose sintering. For example, as shown in Fig. 4, the porosity of S-13 is apparently unaffected by sintering time, whereas that of S-14 markedly decreases between 30 and 60 min.

Significant loss of surface area with increased sintering time is observed for both powders (Fig. 5); however, it would be unwise to attach too much emphasis to these results at this stage, in view of the fact that the porous mass is recessed in the screen. Complete examination of these variables of the thicker plaque now being prepared is in progress.

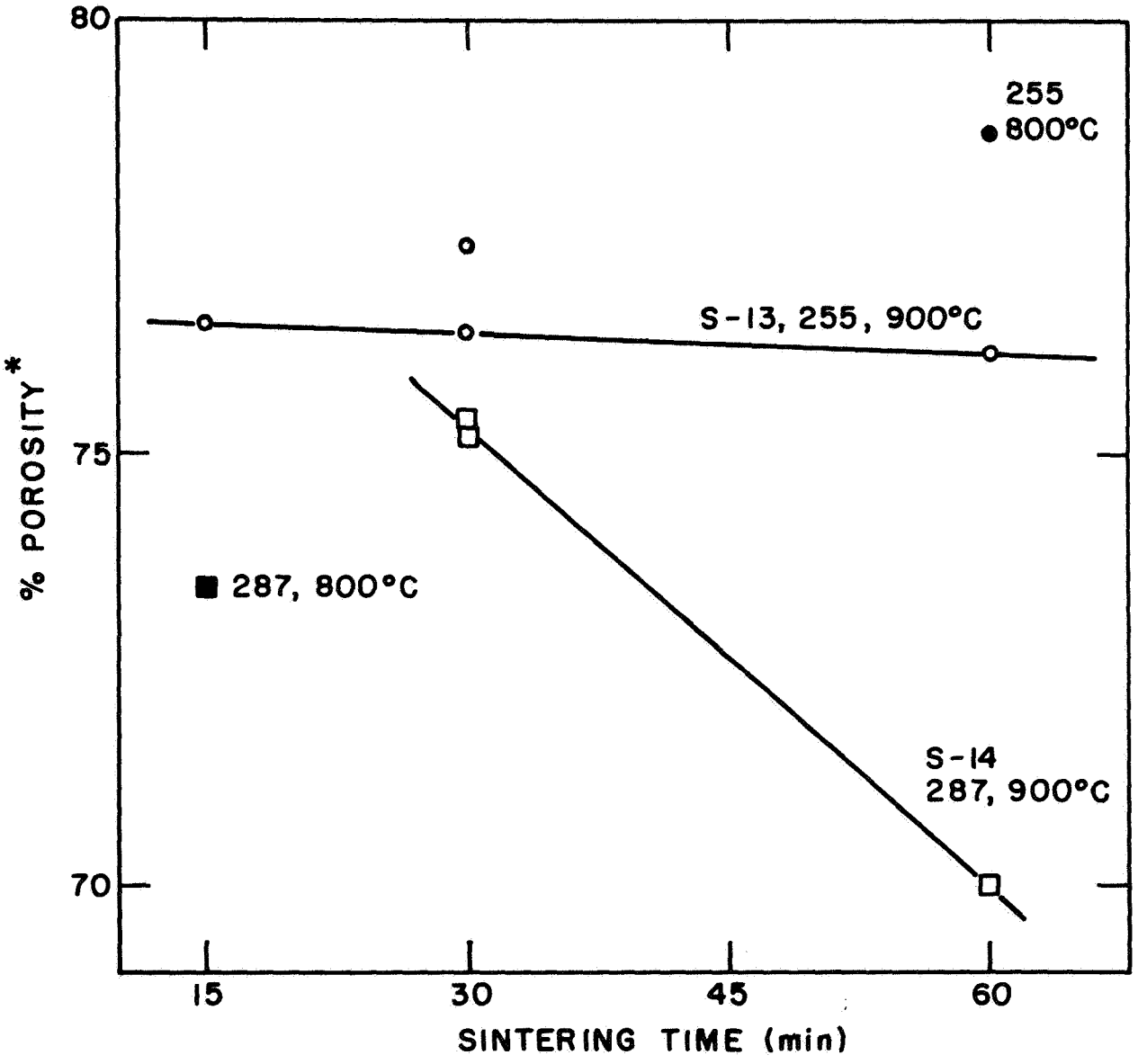

Fig. 4. Porosity versus sintering time (values from mercury porosimetry data)

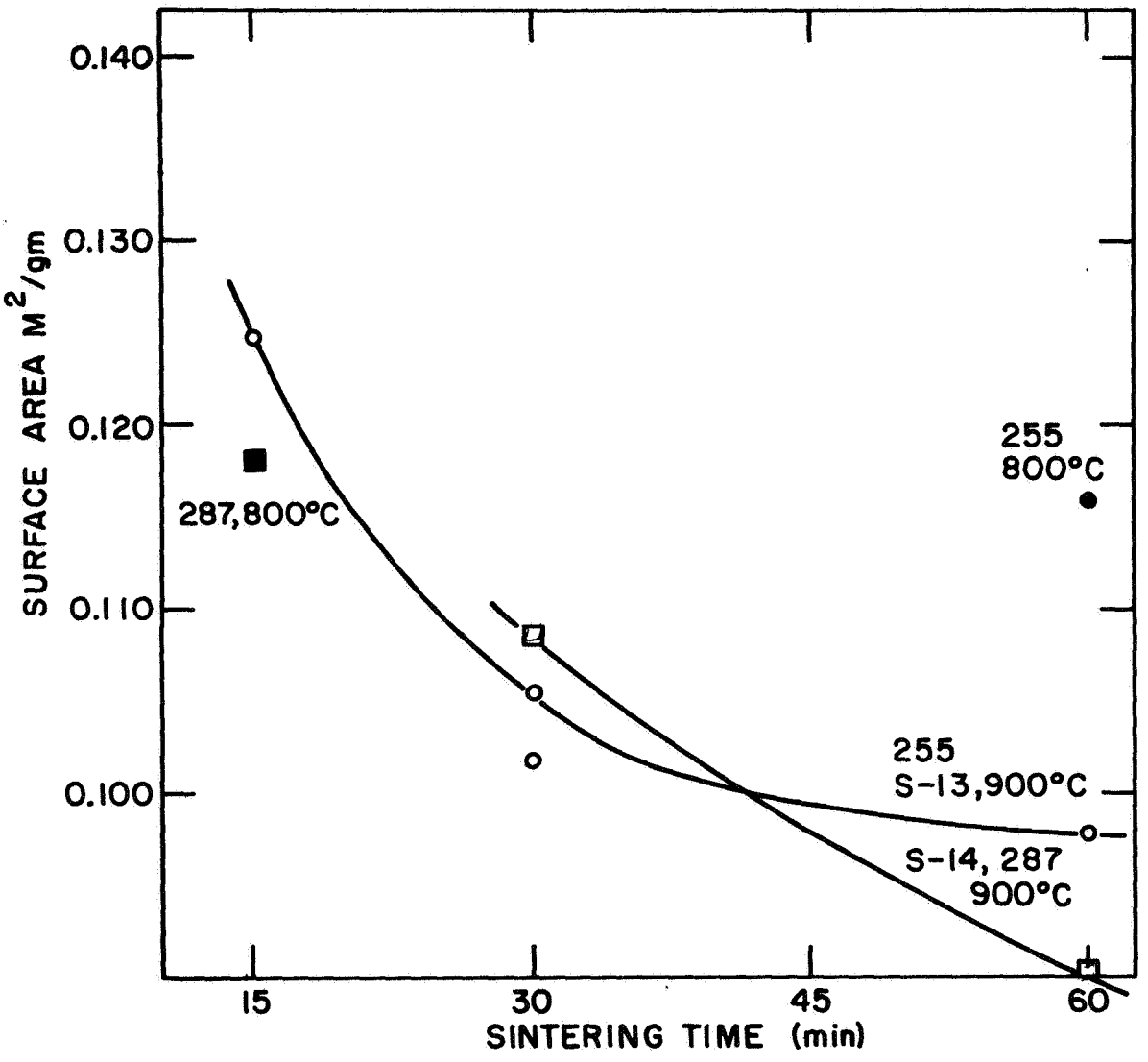

Fig. 5. Surface area of porous mass versus sintering time

V. CHARACTERIZATION OF BASF CARBONYL NICKEL POWDER

A sample of BASF carbonyl nickel powder, as used by SAFT for the manufacture of aerospace battery plaques, was characterized and compared with the INCO carbonyl powders. The results, presented in Table VIII, indicate that the BASF powder is not significantly different from INCO type 255.

Table VIII. Comparison of BASF and Carbonyl Nickel Powders

	Bulk Density, g/cm^3	Surface Area, m^2/g	Fisher No., μ
BASF	0.52	0.518	3.05
Type 255	0.63	0.507	2.78
Type 287	0.95	0.446	3.14

Particle Size Distribution, Weight % in Range

	5—7μ	7—9μ	9—11μ	11—13μ	13—15μ	15—17μ	17—19μ	19μ+
BASF	6.5	11	14	18	16	17	13	
Type 255	9	12.5	15	17	19	20	35	
Type 287	8	11	12.5	14.5	15	13	10	10